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Rate constant and branching fraction for the reaction of O⁺(²D,²P) with CO₂

A. A. Viggiano, Robert A. Morris, ^{a)} and John F. Paulson Geophysics Laboratory (AFSC), Ionospheric Physics Division (LID), Hanscom Air Force Base, Massachusetts 01731-5000

(Received 21 March 1990; accepted 5 April 1990)

The reaction

$$O^{+}(^{4}S) + CO_{2} \rightarrow O_{2}^{+} + CO + 1.19 \text{ eV}$$
 (1a)

$$\rightarrow CO_{2}^{+} + O - 0.2 \text{ eV}$$
 (1b)

has been extensively studied. ¹⁻¹² Reaction (1a) is known to be fast ¹² although it is spin forbidden. ³ At room temperature, reaction (1b) is slow due to the endothermicity of the reaction. ^{13,14} However, as the energy or temperature of the reactants is raised the charge transfer channel becomes important even though the overall rate constant changes only slightly. ^{6,15,16}

Recently, it has been determined that most of the O_2^+ produced in reaction (1a) is vibrationally excited. ¹¹ This has important implications for the atmospheres of Venus and Mars as well as for chemical releases in the earth's atmosphere. ¹⁶

While it is well established that kinetic energy drives the endothermic charge transfer, the influence of other forms of energy is not known. O⁺ has two metastable states, O⁺(2D) and O⁺(2P), which are 3.3 and 5.0 eV above the ground O⁺(4S) state, respectively. ¹⁷ The lifetimes of both of these states are long (>5 s). ¹⁸ Either state has sufficient energy to drive the charge transfer channel, which is endothermic by only 0.2 eV. ^{13,14} In this Note we report the rate constant and branching ratio for the reaction of an unknown mixture of these states with CO₂.

$$O^{+}(^{2}D,^{2}P) + CO_{2} \rightarrow O_{2}^{+} + CO$$
 (2a)

$$\rightarrow CO_2^+ + O. \tag{2b}$$

The measurements were performed in a selected ion flow tube incorporating a monitor ion inlet. The apparatus has been described in detail elsewhere 19,20 and only details pertinent to the present experiment are given here. A mixture of excited states $O^+(^2D,^2P)$ and ground state $O^+(^4S)$ was formed in an electron impact ion source from CO_2 . The mixture of states is unknown. O^+ ions (all three states) were mass selected and injected into a helium buffer. The ions were carried down the flow tube by the helium and sampled by a downstream mass spectrometer.

Rate constants for $O^+(^2D,^2P)$ reacting with CO_2 were measured using the monitor ion technique. ²⁰ This method involves injecting CO just in front of the sampling orifice (1 cm from the orifice). This converts the $O^+(^2D,^2P)$ ions to CO^+ by the fast reaction ¹⁸

$$O^{+}(^{2}D,^{2}P) + CO \rightarrow CO^{+} + O.$$
 (3)

 $O^+(^4S)$ does not react with CO. ¹⁸ This allows monitoring of the excited state signal by converting the $O^+(^2D,^2P)$ signal, which is only a fraction of the signal at 16 daltons, into a signal that is monitored at 28 daltons. The decay of the CO^+ , which is thus proportional to the decay of the $O^+(^2D,^2P)$, was then monitored as a function of the CO_2 flow rate, and rate constants were derived in the normal manner. ¹⁹ The rate constant for $O^+(^4S)$ reacting with CO_2 was also measured in the normal manner, except that CO was added upstream of the reaction region in order to eliminate $O^+(^2D,^2P)$ ions from contributing to the 16 amu ion signal.

The products from $O^+(^2D,^2P)$ reacting with CO_2 were determined as follows. The percentage of $O^+(^2D,^2P)$ in the total ion signal at 16 daltons was determined by monitoring the decay of that total ion signal as CO was added. Both He and CO are known not to quench the excited states, 18 and CO is therefore a good monitor of the excited state fraction of the O⁺ signal along the whole length of the flow tube. Upon addition of CO, 6% of the O⁺ reacted to form CO⁺, indicating that 6% of the total O+ signal was due to excited states. The reaction of O+(4S) with CO2 produces only O2+ at 300 K. 9,12 Production of O2+ and CO2+ was monitored as a function of CO, flow rate when all O + states were present. The products of the excited state reaction were then determined by comparing the percentage of CO₂⁺ produced to the amount of $O^+(^2D,^2P)$ determined by the CO monitor method. Mass resolution was kept low to avoid mass discrimination problems.

The overall rate constants for reactions 1 and 2 were both found to be 1.06×10^{-9} cm³ s⁻¹. The uncertainty is estimated to be $\pm 25\%$. The ratio of the rate constants is believed to be accurate to 5%. This reflects only the uncer-

tainty in measuring the decay of the ion signal as a function of the CO_2 flow. All other errors cancel since the experimental conditions were the same for both rate constant determinations. The rate constant for reaction 1 is found to be in good agreement with previous measurements which range form 0.9 to 1.1×10^{-9} cm³ s⁻¹. ¹² The collision rate constant is 1.17×10^{-9} cm³ s⁻¹ for both reactions. ²¹

When CO_2 was added to the mixture of all three states of O^+ in the flow tube, 5.7% of the product ions were CO_2^+ , the remainder being O_2^+ . This compares to a total of 6.0% of the O^+ ions in the 2D and 2P excited states. This implies that 95% of reaction 2 proceeds by charge transfer (2b). As stated above the resolution of the mass spectrometer was kept low for this determination, and therefore little mass discrimination was present. A small degree of mass discrimination may have affected this determination, which would then favor the lighter O_2^+ ion. We therefore report our finding as a lower limit, i.e., $\geqslant 95\%$ of the reaction proceeds by charge transfer.

It is interesting that both the ground and excited states of O+ react with the same rate constant and that this rate constant is not quite equal to the collisional rate constant. We believe that the reactions do proceed at less than the collisional rate constant, even though our measurements are equal to the collision rate constant within experimental error. This belief is based on the fact that the rate constant for the ground state reaction has been measured by a number of groups and all of the measurements are slightly below the collision rate constant. 12 Since we found the rate constant for the excited state to be equal to that of the ground state with little uncertainty, we feel that the rate constant for the excited state is also below the collisional limit. A mechanism that would cause different O + states with greatly different energies and angular momenta to react with the same efficiency would probably depend only on some property of CO2. One possibility is an orientation effect. The answer to this question is beyond the scope of this paper.

Electronic energy in the O $^+$ changes the product of the reaction from 100% O_2 to >95% CO_2 . The electronic

energy is more than 3 eV higher than the energy necessary to drive the endothermic charge transfer. This is in accord with the fact that kinetic energy also efficiently drives the charge transfer when enough energy is available. 6,15,16 Based on the above, one would also expect other forms of energy to drive the charge transfer channel. Future experiments in our laboratory are designed to explore the influence of CO_2 vibrations on the branching ratio between O_2^+ and CO_2^+ in reaction 1.

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